



## Sensitivity improvement of thin-film techniques by micro-sample analysis.

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## Context

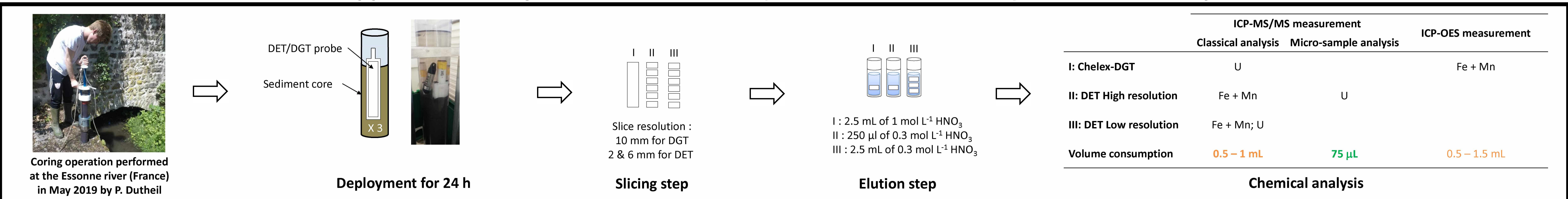
DET (Diffusive Equilibrium in Thin film) and DGT (Diffusive Gradient in Thin film) techniques have been developed in the 90's to sample dissolved elements. They are of great interest to study diagenetic processes at the water/sediment interface.

Whereas DGT allows on field preconcentration of element on a binding gel, DET is limited to the equilibrium between the solution and an hydrogel. Both approaches require an elution step for chemical analyses. The elution volume depends on the analytical tool consumption (0.5 to 5 mL for elemental analysis) and may be critical for trace and ultra trace element determination with DET. Then preconcentration in DGT facilitates analytical step, especially for small volume samples like pore water. Nevertheless DGT advantage may be reduced by several parameters like competition on binding gel or evolution of diffusion coefficient over time or with temperature.

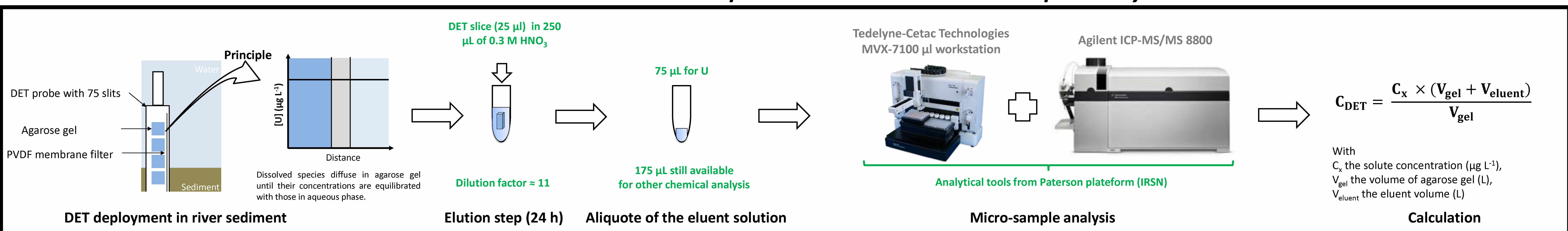
**The objective of the present work was to overpass the DET limits to produce high resolution depth profiles of uranium in pore water of a river sediment.**

The strategy is based on micro-sample analysis with the Tedelyne-Cetac Technologies MVX 7100 mL workstation hyphenated to the Agilent 8800 Inductively Coupled Plasma – Tandem Mass Spectrometry

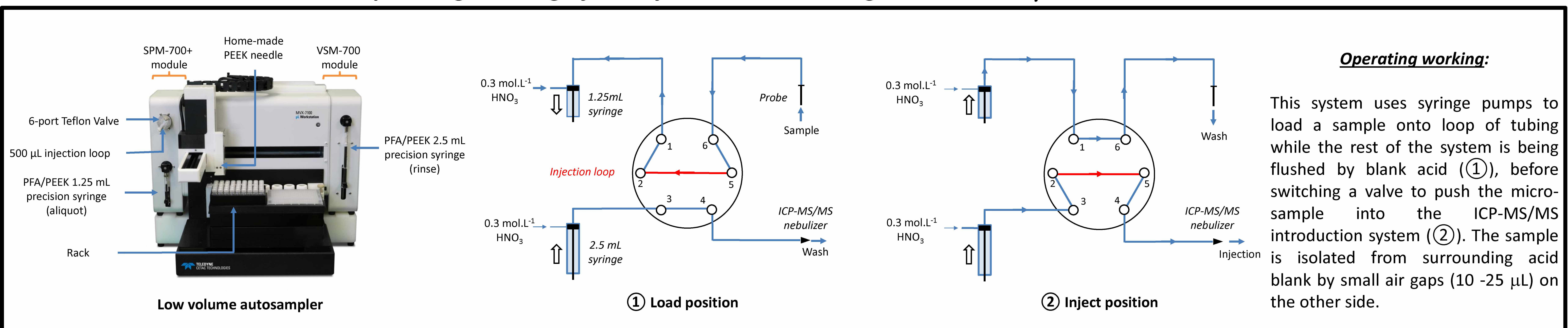
**Field application: comparison between DET (two resolutions tested) and Chelex DGT procedures**



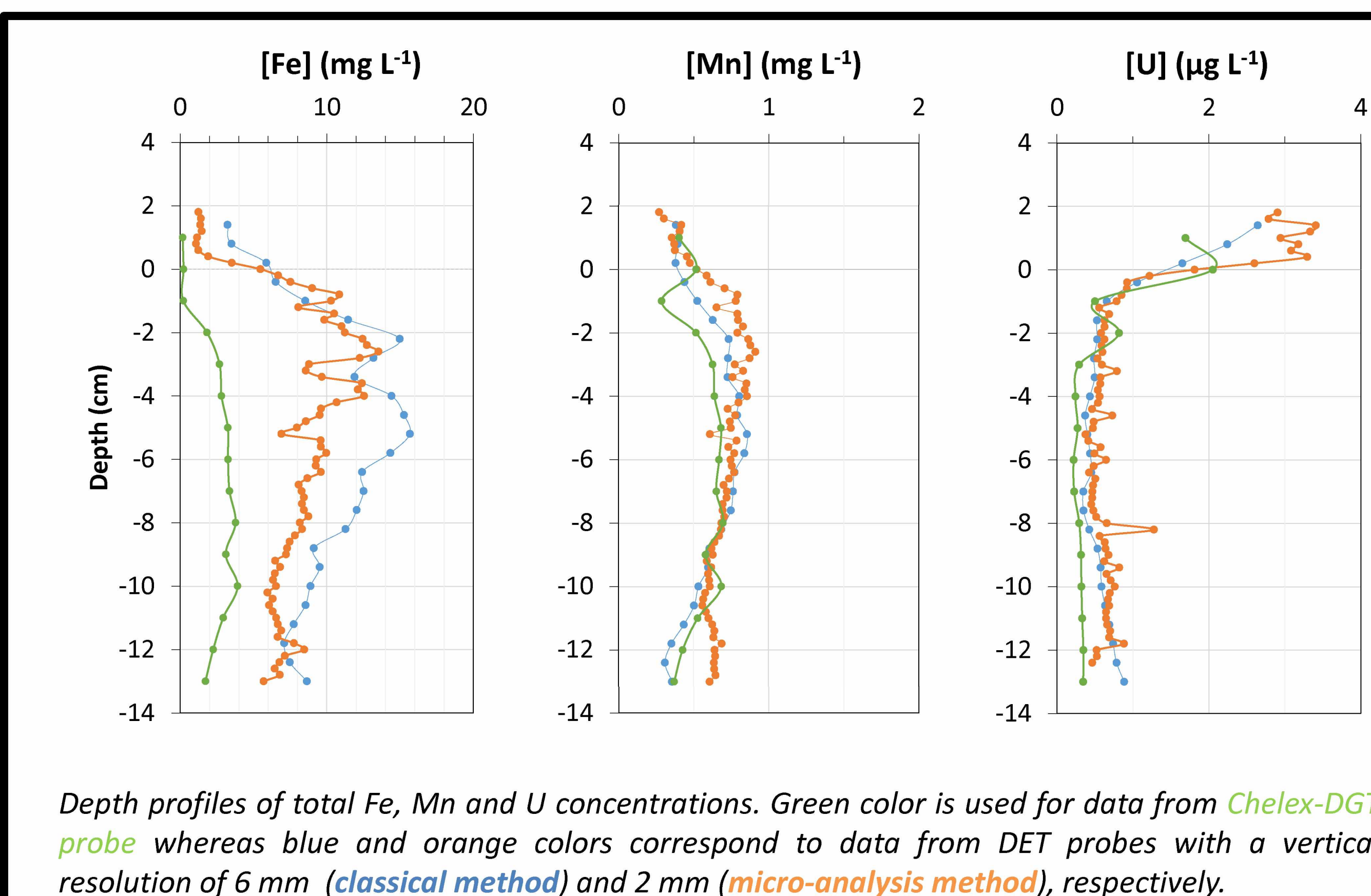
***Focus on DET techniques associated to micro-sample analysis***



### ***Operating working of Tedelyne-Cetac Technologies MVX-7100 $\mu$ L workstation***



## Results and discussion



The DET profiles (orange and blue) are similar whatever the resolution. The lateral shift is probably linked to sediment heterogeneity in the sediment core.

The new DET procedure is consequently suitable to analyze uranium concentration at trace levels. Its sensitivity is improved by using the micro-sample analysis. It could be again possible to minimize the elution volume and MVX-7100  $\mu\text{L}$  – ICP-MS/MS parameters.

Geochemical interpretation:

The combined use of DET and DGT allows to estimate the available stock of elements in sediment. In our example it is very low for Fe and limited for U. On the contrary the Mn stock is totally available.

Reductive and/or dissolution zone of iron and manganese (hydr)-oxides is occurring in the sediment core. Regarding U profiles, a gradual decrease in concentration is observed in the first cm of depth before stabilizing to 0.5 – 0.6 mg L<sup>-1</sup>. It is supposed that there is reductive precipitation of U(VI) to U(IV) after its diffusion in sediment compartment.

## Conclusion and perspectives

This study has shown the possibility to improve the sensitivity of DET techniques. The elution volume is reduced to 250  $\mu\text{L}$ . 75  $\mu\text{L}$  are used to obtain a high resolution depth profile of uranium concentration in the sediment of the Essonne river, and 50  $\mu\text{L}$  for those of iron and manganese concentration.

This work opens new opportunities to produce high resolution geochemical data at the water/sediment interface.

Our research team is open to collaboration on many topics:

- Impact of radioactive waste storage and uranium mining activities;
- Pre-concentration/purification technique (Cs, I, Pb, Ra, Th, U, etc.);
- Speciation measurement (passive samplers, IC-ICP-MS, etc.).

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## Acknowledgements

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